

Measurement of the Vaporization Enthalpy of Complex Mixtures by Correlation-Gas Chromatography. The Vaporization Enthalpy of RP-1, JP-7, and JP-8 Rocket and Jet Fuels at $T = 298.15$ K

James S. Chickos* and Hui Zhao

Department of Chemistry, University of Missouri-St. Louis, St. Louis, Missouri 63121

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The use of correlation-gas chromatography to measure the vaporization enthalpy $\{\Delta_v^{\#}H_m(298.15\text{ K})\}$ of complex fuels is demonstrated using RP-1, JP-7, and JP-8, which are all rocket and jet fuels. Vaporization enthalpies of 308, 341, and 441 kJ/kg have been obtained assuming average compositions of $C_{12}H_{23.4}$, $C_{12}H_{25}$, and $C_{11}H_{21}$, respectively. The H/C ratio in these fuels has been measured by 1H NMR, and an average molecular weight has been determined using gas chromatography. Some variance in composition with the literature values has been observed. The vaporization enthalpies are compared to those in the literature and to values estimated for these compositions. The estimated values are discussed in terms of the composition of the fuel. The effect of detector bias in evaluating the mole fraction of each hydrocarbon present, as a function of size, is tested and determined to have a relatively small effect on the vaporization enthalpy.

Introduction

Aviation fuel has two important roles in advanced aircraft. The first and most obvious role is for propulsion.¹ A second and increasingly important role is as an airframe coolant. A considerable amount of interest has focused on the development of fuels that, when heated, undergo endothermic decomposition to yield secondary products whose combustion is used for propulsion.^{2–4} The catalytic dehydrogenation of methylcyclohexane to toluene and hydrogen is an example of an endothermic reaction identified in early investigations of endothermic fuels.⁵ Another important source of cooling is heat uptake during the vaporization of the fuel from the condensed phase to the gas phase. The endothermicity of the gas-phase dehydrogenation of methylcyclohexane—2.1 kJ/g (205 kJ/mol)⁶—can be compared to an endothermicity of 0.36 kJ/g (35.4 kJ/mol), which is associated with the liquid-to-gas phase change when both processes occur at $T = 298.15$ K. Ignoring

the heat necessary to raise the fuel to the temperature at which the dehydrogenation reaction proceeds readily, the phase change contributes an additional 16% to the total endothermicity of the process. Most fuels currently in use are complex mixtures of hydrocarbons. Until recently, the total vaporization enthalpy of such a mixture could only be measured by a vaporization calorimeter, such as a Calvet calorimeter. Physical property data on fuel properties include a variety of properties such as heating value, specific gravity, critical temperature and pressure, boiling range, etc. Notably absent from this list is the vaporization enthalpy.

A simple technique, called correlation-gas chromatography, was recently applied to the evaluation of the vaporization enthalpy of RJ-4, which is a high-energy-density rocket fuel, consisting of a mixture of exo- and endo-dimethyltetrahydrodicyclopentadienes.⁷ In this article, the technique of correlation-gas chromatography is applied to evaluate the vaporization enthalpies of the more-complex hydrocarbon fuels RP-1, JP-7, and JP-8. The values evaluated in this correlation are subject to the uncertainty associated in assuming ideal enthalpies of mixing ($\Delta H_{\text{mix}} = 0$). Although vaporization enthalpies of these fuels will be dependent on the origin of the sample and its history, a comparison of vaporization enthalpies obtained by correlation-gas chromatography to those values available in the literature, either by estimation or measurement, would be informative.

* Author to whom correspondence should be addressed. Telephone: 314 516 5377. Fax: 314 516 5342. E-mail: jsc@umsl.edu.

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69 Correlation-gas chromatography has been used fre-
 70 quently to measure the vaporization enthalpy of pure
 71 compounds.⁸ The technique consists of recording the
 72 retention time of an analyte, as a function of tempera-
 73 ture. The retention time (t), adjusted for the dead
 74 volume of the column by subtracting the retention time
 75 of a nonretained reference, measures the amount of time
 76 the analyte spends on the column (t_a) and is inversely
 77 proportional the analyte's vapor pressure on the column.
 78 A typical graphical depiction of $\ln(1/t_a)$ vs $1/T$ (where
 79 temperature T is given in Kelvin) results in a linear plot
 80 with a slope equal to $-\Delta_{\text{sln}}^{\text{g}}H_m(T_m)$, when multiplied by
 81 the gas constant, R . The enthalpy term, $\Delta_{\text{sln}}^{\text{g}}H_m(T_m)$, is
 82 simply the enthalpy of transfer of the analyte from the
 83 column to the vapor at the mean temperature of
 84 measurement. Because the analyte, in dilute form, is
 85 dissolved or adsorbed on the stationary phase of the
 86 column, it does not matter whether the analyte is a solid
 87 or a liquid.⁹ When the vaporization enthalpies of a
 88 mixture of analytes with known vaporization enthalpies
 89 $\{\Delta_i^{\text{g}}H_m(T)\}$ are correlated with their respective enthal-
 90 pies of transfer $\{\Delta_{\text{sln}}^{\text{g}}H_m(T_m)\}$, a linear correlation is
 91 obtained. If the prepared mixture also contains several
 92 structurally related components with unknown vapor-
 93 ization enthalpies, the linear relationship observed
 94 between $\Delta_i^{\text{g}}H_m(T)$ and $\Delta_{\text{sln}}^{\text{g}}H_m(T_m)$ can be used to obtain
 95 the vaporization enthalpies that are unknown. Although
 96 this technique has been used primarily to obtain vapor-
 97 ization enthalpies at $T = 298.15$ K, in principle, it
 98 can be used to obtain vaporization enthalpies at any
 99 temperature T , provided the vaporization enthalpies of
 100 all the standards are referenced to the same tempera-
 101 ture. In the case of JP-7 and JP-8 fuels, the n -alkanes
 102 that are used as standards are present naturally in the
 103 fuel at sufficiently high levels to facilitate their identi-
 104 fication. Vaporization enthalpies of the n -alkanes are
 105 available and can be calculated over a broad range of
 106 temperatures.¹⁰ In the case of RP-1 fuel, it was neces-
 107 sary to add external references.

108 Application of this technique to a complex mixture
 109 follows directly from the temperature dependence of the
 110 retention time. Consider a mixture of i hydrocarbon
 111 components. For each component detected by the gas
 112 chromatograph, either individually or as a multiple
 113 component peak, the following relationships apply:

$$\begin{aligned} \ln(1/t_{a1}) &= \ln(A_1) - \frac{\Delta_{\text{sln}}^{\text{g}}H_m(T_m)_{(1)}}{RT} \\ \ln(1/t_{a2}) &= \ln(A_2) - \frac{\Delta_{\text{sln}}^{\text{g}}H_m(T_m)_{(2)}}{RT} \\ \dots & \\ \ln(1/t_{ai}) &= \ln(A_i) - \frac{\Delta_{\text{sln}}^{\text{g}}H_m(T_m)_{(i)}}{RT} \end{aligned} \quad (1)$$

(8) For some recent examples, see: Bashir-Hashemi, A.; Chickos, J. S.; Hanshaw, W.; Zhao, H.; Farivar, B. S.; Liebman, J. F. The enthalpy of sublimation of cubane. *Thermochim. Acta* **2004**, *424*, 91–97 and references cited therein.

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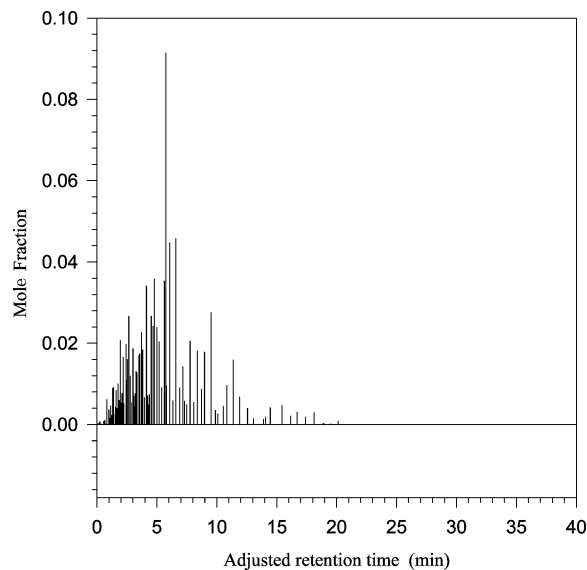


Figure 1. Bar graph of the mole fraction versus retention time of RP-1 fuel at 384 K without standards. The retention time of the solvent CH_2Cl_2 ($t = 0$) is not shown.

Multiplying each component by its mole fraction and summing over all i components results in the following equation: 115 116 117

$$\sum_i n_i \ln(1/t_{ai}) = \sum_i n_i \ln(A_i) - \sum_i n_i \left\{ \frac{\Delta_{\text{sln}}^{\text{g}}H_m(T_m)_{(i)}}{RT} \right\} \quad (2)$$

where 118

$$\sum_i n_i \{\Delta_{\text{sln}}^{\text{g}}H_m(T_m)_{(i)}\} = \Delta_{\text{sln}}^{\text{g}}H_m(T_m)_{\text{mix}} \quad (3)$$

The enthalpy term on the extreme right, $n_i\{\Delta_{\text{sln}}^{\text{g}}H_m(T_m)_{(i)}\}$, is the enthalpy of transfer from solution to the vapor of the entire mixture, $\Delta_{\text{sln}}^{\text{g}}H_m(T_m)_{(\text{mix})}$. A plot of the sum of $n_i \ln(1/t_{ai})$ versus $1/T$ should result in a straight line with a slope of $-\Delta_{\text{sln}}^{\text{g}}H_m(T_m)_{(\text{mix})}/R$. If, in addition to the mixture of i components, several structurally related standards are also included in the mixture, a plot of $\ln(1/t_a)$ versus $1/T$ for each standard should also result in a linear plot. The $\Delta_{\text{sln}}^{\text{g}}H_m(T_m)$ term for each standard can be correlated to its respective vaporization enthalpy, as described previously. From the correlation equation and the $\Delta_{\text{sln}}^{\text{g}}H_m(T_m)_{(\text{mix})}$ of the mixture, the vaporization enthalpy of the ensemble, $\Delta_i^{\text{g}}H_m(T)_{\text{mix}}$, can be determined. 119 120 121 122 123 124 125 126 127 128 129 130 131 132

The RP-1, JP-7, and JP-8 fuels are complex mixtures of hydrocarbons.¹¹ Typical compositions are reproduced in Figures 1–3. These figures represent the composition as a function of retention time in the form of a bar graph. Each peak evaluated by the integrator is plotted as a function of its mole fraction. Each peak represents either a single substance or a mixture of substances with indistinguishable retention times. These figures 133 134 135 136 137 138 139 140

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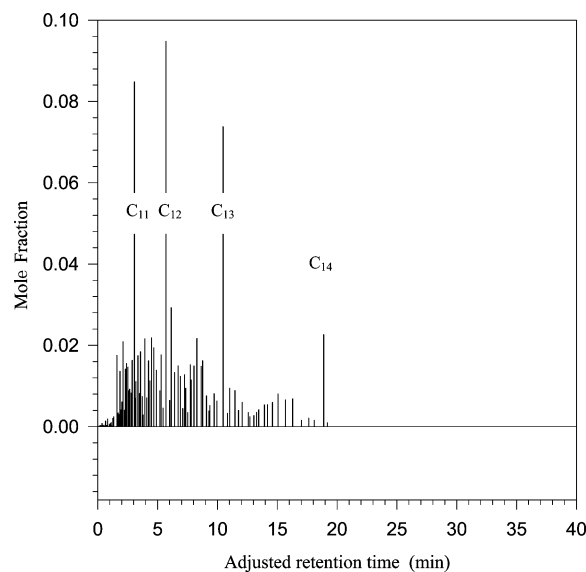


Figure 2. Bar graph of the mole fraction versus retention time of JP-7 fuel at 385 K. The retention time of the solvent, CH_2Cl_2 ($t = 0$), is not shown. The n -alkanes, used as internal standards, are among the most abundant hydrocarbons in JP-7 fuel.

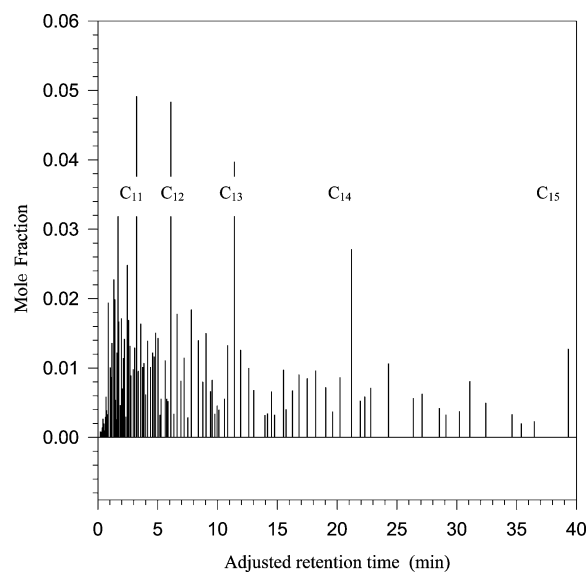


Figure 3. Bar graph of the mole fraction versus adjusted retention time of JP-8 fuel at 384 K. The retention times of the solvent, CH_2Cl_2 ($t = 0$), are not shown. The n -alkanes, which are used as internal standards, are among the most-abundant hydrocarbons in JP-8 fuel.

can be compared to similar chromatograms obtained by gas chromatography–mass spectroscopy (GC/MS).⁴ The chromatograms in Figures 1–3 were obtained at approximately the same temperature. As indicated in the graphs, the relative volatilities of the components decrease in going from RP-1 to JP-7 to JP-8. The n -alkanes seem to be among the most abundant hydrocarbons present in JP-7 and JP-8 fuels, and these components, once identified by GC/MS studies, were used as the internal standards. Fuel compositions will vary from batch to batch.¹¹ Consequently, the vaporization enthalpies reported in this communication should be viewed as representative values. The Supporting Information that accompanies this publication should provide an interested party sufficient detail to reproduce the protocol that is described.

Experimental Section

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Samples of RP-1, JP-7, and JP-8 fuels were kindly supplied by Tim Edwards at Wright–Patterson Air Force Base in Ohio. (The samples correspond to sample lot numbers POSF 4220, 3327, and 3773, respectively.) The following compounds were used as vaporization enthalpy standards for RP-1 fuel: octane, 1-nonene, decane, naphthalene, dodecane, and tridecane. For RP-1 fuel, these were added as external standards, and the RP-1 was analyzed as a mixture. The contribution of the standards to the mole fraction at the appropriate retention time was subtracted using the spectrum of a sample of RP-1 without external standards. Samples of JP-7 and JP-8 fuel already contain substantial amounts of n -alkanes, as identified by GC/MS and retention time studies. n -Undecane, n -dodecane, n -tridecane, and n -tetradecane were identified and used as internal standards for JP-7 fuel and hydrocarbons n -decane through n -pentadecane were similarly identified and used as standards in JP-8 fuel. The retention times of most of these compounds are identified in Figures 1–3. The vaporization enthalpies of the compounds used as standards are well-known.^{12,13}

The mass spectra were recorded on a Hewlett–Packard model HP 5988A GC/MS system. The n -alkanes were identified by comparison of their mass spectra to authentic spectra available in a standard database.¹⁴ Correlation-gas chromatography experiments were performed on a Hewlett–Packard model HP 5890A Series II gas chromatograph that was equipped with a split/splitless capillary injection port and a flame ionization detector run at a split ratio of $\sim 100/1$. Retention times were recorded to three significant figures following the decimal point on an enhanced Chemstation G1701BA, Version B01.00. The instrument was operated isothermally, using a 30-m SPB-5 capillary column. Helium was used as the carrier gas. The retention time of the solvent (CH_2Cl_2) was used as a measure of the nonretained reference. Adjusted retention times (t_a) were calculated by subtracting the measured retention time of each analyte from the retention time of the nonretained reference, as a function of temperature over a 30-K range. Column temperatures were controlled by the gas chromatograph and were monitored independently, using a Fluke model 51 K/J thermometer. Temperature was maintained constant to ± 0.1 K. The purities of the other standards were high (0.99 mol fraction). The results for RP-1 fuel using integrator intensities directly without corrections, as well as attempts to correct for detector bias, are reported in Table 1. Similar data for JP-7 and JP-8 fuel are available in the tables provided in the Supporting Information. Uncertainties in the vaporization enthalpies reported for the RP-1, JP-7, and JP-8 fuels in Tables 3 and 6 (shown later in this work) refer to the precision of the measurements and represent two standard deviations associated with the intercept of eqs 5–7. All other uncertainties represent two standard deviations. The accuracy associated with the vaporization enthalpies is more difficult to ascertain, because these analyses are performed on complex mixtures. We would estimate these values to be accurate within ± 4 kJ/mol (95% confidence level).

NMR spectra were measured on a Bruker model Avance 300 NMR spectrometer using deuteriochloroform as the solvent. The ratio of aromatic and olefinic hydrogens (δ 6.5–8.5 ppm) to aliphatic hydrogens (δ 0.5–3.5 ppm), as determined by integration, varied from $1/_{831}$ for JP-7 and $1/_{119}$ for RP-1 to $1/_{28}$ for JP-8. The average hydrogen/carbon (H/C) ratio in the fuel samples used was also evaluated by integration of the ^1H NMR

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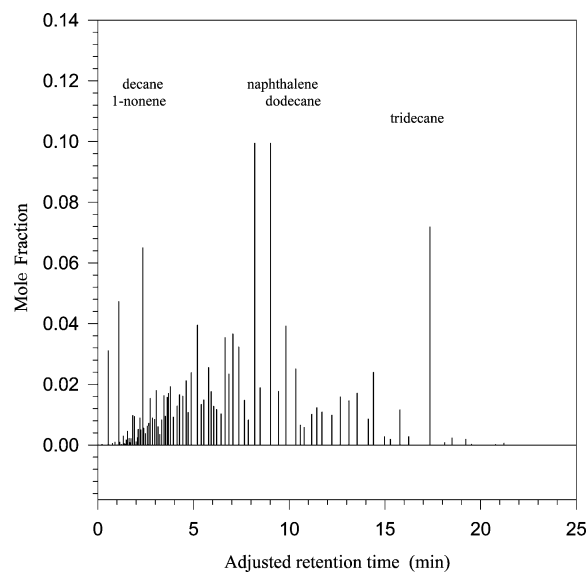


Figure 4. Bar graph of the mole fraction versus retention time of RP-1 fuel at 369 K with standards. The retention time of the solvent, CH_2Cl_2 ($t = 0$), is not shown.

220 spectra. In this instance, an external reference, dimethyl
 221 phthalate (DMP), was used as the reference. The number of
 222 moles of hydrogen in the fuel sample used ($\text{mol}_{\text{H fuel}}$) could be
 223 evaluated using eq 4:

$$\text{mol}_{\text{H fuel}} = \frac{\bar{n}_{\text{H}} m_{\text{fuel}}}{\text{MW}_{\text{fuel}}} = \frac{\bar{n}_{\text{C}} (\text{H/C}) m_{\text{fuel}}}{\bar{n}_{\text{C}} [12 + (\text{H/C})]} = \frac{(\text{H/C}) m_{\text{fuel}}}{12 + (\text{H/C})} \quad (4)$$

224 The total number of moles of hydrogen is dependent on the
 225 mass of the fuel (m_{fuel}) used, the average molecular weight
 226 (MW_{fuel}), and the number of hydrogens in the average molec-
 227 ular formula (\bar{n}_{H}). The average molecular weight of the fuel
 228 can be expressed in terms of the average number of carbons
 229 (\bar{n}_{C}), the H/C ratio, and each respective atomic weight. Upon
 230 simplification of eq 4, the number of moles of hydrogen is
 231 dependent only on the mass used and the H/C ratio. The total
 232 number of moles of hydrogen in the methoxy groups of
 233 dimethyl phthalate could also be evaluated by the mass used,
 234 its molecular weight, and a statistical factor of 6. Because the
 235 H/C ratio is the only unknown in the $\text{mol}_{\text{H fuel}}/\text{mol}_{\text{H DMP}}$ ratio
 236 determined experimentally via NMR, it can be evaluated from
 237 this relationship. This experiment was repeated for the JP-7
 238 and JP-8 fuels. The results are summarized in Table 8, which
 239 is given later in this work; additional details are provided in
 240 the Supporting Information.

241 Results

242 The detailed calculations for RP-1 fuel are given as
 243 an example of the analytical procedure used to determine
 244 the vaporization enthalpy. Analysis of this sample
 245 represents the most complex situation, because the

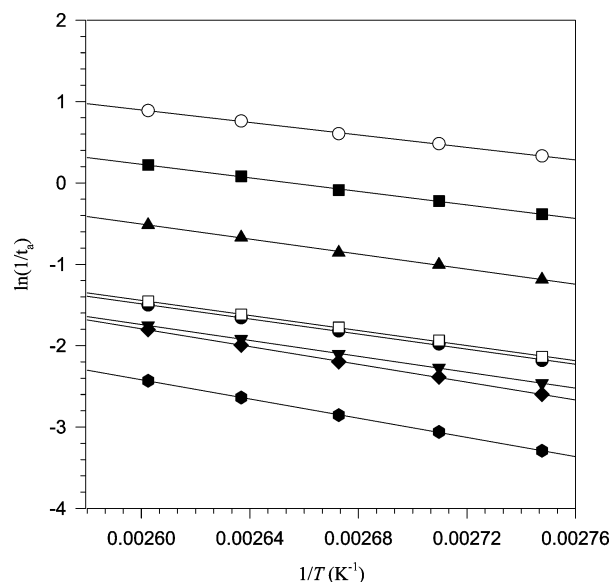


Figure 5. Plot of the natural logarithm of the reciprocal adjusted retention times versus $1/T$ for (from top to bottom) (○) octane, (■) 1-nonene, (▲) decane, (●) RP-1 (raw data), (□) RP-1 (adjusted for detector bias), (▼) naphthalene, (◆) dodecane, and (●) tridecane.

standards used are not present internally in the fuel in 246
 sufficient concentration to be useful. Figure 4 illustrates 247
 a typical chromatograph of the RP-1 fuel with the 248
 internal standards present. The retention times of the 249
 internal standards are reported in Table 2. 250

A plot of $\ln(1/t_a)$ versus $1/T$ for the RP-1 fuel results 251
 in Figure 5. The slopes and intercepts of these lines are 252
 provided in the second and third columns of Table 3. 253
 Enthalpies of transfer from the stationary phase of the 254
 column to the gas phase at the mean temperature of 255
 measurement, $\Delta_{\text{sln}}^{\text{g}} H_m(368 \text{ K})$, were obtained by multi- 256
 plying the slope of the line by the gas constant (R). 257
 A plot of $\Delta_{\text{sln}}^{\text{g}} H_m(368 \text{ K})$ versus the vaporization enthal- 258
 pies of the standards, $\Delta_{\text{sln}}^{\text{g}} H_m(298.15 \text{ K})$, results in eq 5, 259
 which is given at the bottom of the RP-1 portion of Table 260
 3. This equation was used to evaluate the vaporization 261
 enthalpy of RP-1 fuel. 262

The mole fraction of each component in RP-1 was 263
 calculated two ways. The area generated by the detector 264
 response (A_i) was summed over all i components and 265
 used to calculate the mole fraction of each component. 266
 This sum, $\sum A_i$, is reported at the bottom of the data sets 267
 in Table 1 for each temperature studied. Multiplication 268
 of the mole fraction of each component according to eq 269
 1 and summing the results over all components at each 270
 temperature investigated resulted in values of $\sum n_i \ln-$ 271
 $(1/t_{ai})$, which were then plotted as a function of reciprocal 272
 temperature ($1/T$). The results of this plot are illus- 273

Table 2. Unadjusted Retention Times of the Standards Used in RP-1 Fuel

compound	Unadjusted Retention Time, t (min)				
	$T = 364.0 \text{ K}$	$T = 369.1 \text{ K}$	$T = 374.2 \text{ K}$	$T = 379.3 \text{ K}$	$T = 384.3 \text{ K}$
CH_2Cl_2	0.583	0.579	0.569	0.563	0.564
octane	1.301	1.196	1.115	1.03	0.975
1-nonene	2.052	1.827	1.661	1.484	1.367
decane	3.857	3.31	2.921	2.517	2.238
naphthalene	12.307	10.269	8.763	7.384	6.32
dodecane	14.038	11.452	9.591	7.912	6.631
tridecane	27.458	21.914	17.921	14.546	11.94

Table 3. Slopes, Intercepts, Enthalpies of Transfer, and Enthalpies of Vaporization of the Standards and Those Calculated for RP-1, JP-7, and JP-8 Fuels

For RP-1 Fuel					
	slope	intercept	$\Delta_{\text{sln}}^{\text{g}}H_{\text{m}}(368 \text{ K})$ (kJ/mol)	$\Delta_{\text{f}}^{\text{g}}H_{\text{m}}(298.15 \text{ K})$ (kJ/mol)	
				literature value ^b	calculated value
octane	-3838 ± 78	10.88 ± 0.01	31.91	41.56	41.8
1-nonene	-4162 ± 84	11.05 ± 0.01	34.60	45.5	45.8
decane	-4615 ± 84	11.49 ± 0.01	38.37	51.42	51.3
naphthalene	-4884 ± 48	10.96 ± 0.01	40.60	55.65	54.8
dodecane	-5464 ± 58	12.41 ± 0.01	45.42	61.52	61.7
tridecane	-5897 ± 43	12.91 ± 0.01	49.03	66.68	67.0
RP-1	-4640 ± 100	10.58 ± 0.03	38.57		51.6 ± 1.2
RP-1 ^a	-4626 ± 94	11.58 ± 0.03	38.45		51.5 ± 1.2

$$\Delta_{\text{f}}^{\text{g}}H_{\text{m}}(298.15 \text{ K}) \text{ (kJ/mol)} = (1.472 \pm 0.041)\Delta_{\text{sln}}^{\text{g}}H_{\text{m}}(368 \text{ K}) - (5.145 \pm 0.59); r^2 = 0.9970 \quad (5)$$

For JP-7 Fuel					
	slope	intercept	$\Delta_{\text{sln}}^{\text{g}}H_{\text{m}}(387 \text{ K})$ (kJ/mol)	$\Delta_{\text{f}}^{\text{g}}H_{\text{m}}(298.15 \text{ K})$ (kJ/mol)	
				literature value ^b	calculated value
undecane	-5413.1	12.923	45.004	56.6	55.9
dodecane	-6281.8	15.334	52.227	61.5	62.8
tridecane	-6782.7	16.042	56.391	66.7	66.8
tetradecane	-7311.9	16.849	60.791	71.7	71.0
JP-7	-5635.4	12.964	46.853		57.6 ± 2.3
JP-7 ^a	-5582.3	12.884	45.080		57.2 ± 2.3

$$\Delta_{\text{f}}^{\text{g}}H_{\text{m}}(298.15 \text{ K}) \text{ (kJ/mol)} = (0.961 \pm 0.10)\Delta_{\text{sln}}^{\text{g}}H_{\text{m}}(387 \text{ K}) - (12.63 \pm 2.3); r^2 = 0.9788 \quad (6)$$

For JP-8 Fuel					
	slope	intercept	$\Delta_{\text{sln}}^{\text{g}}H_{\text{m}}(400 \text{ K})$ (kJ/mol)	$\Delta_{\text{f}}^{\text{g}}H_{\text{m}}(298.15 \text{ K})$ (kJ/mol)	
				literature value ^b	calculated value
decane	-4473.6	11.109	37.191	51.4	51.2
undecane	-4823.1	11.373	40.097	56.6	56.4
dodecane	-5185.5	11.682	43.110	61.5	61.9
tridecane	-5526.9	11.945	45.948	66.7	67.0
tetradecane	-5852.1	12.172	48.652	71.7	71.9
pentadecane	-6152.5	12.338	51.149	76.8	76.4
JP-8	-5557.6	12.828	46.204		67.4 ± 1.0
JP-8 ^a	-5416.6	12.602	45.031		65.3 ± 1.0

$$\Delta_{\text{f}}^{\text{g}}H_{\text{m}}(298.15 \text{ K}) \text{ (kJ/mol)} = (1.804 \pm 0.03)\Delta_{\text{sln}}^{\text{g}}H_{\text{m}}(400 \text{ K}) - (15.9 \pm 0.5); r^2 = 0.9989 \quad (7)$$

^a Adjusted for detector bias as described in the text. ^b From refs 12 and 13.

274 trated by the open square symbols in Figure 5. The
275 $\sum n_i \ln(1/t_{ai})$ values are also reproduced at the bottom of
276 the data sets in Table 1 at each temperature.

277 This method of evaluating the mole fraction of each
278 component assumes that the detector response is not
279 biased, in regard to molecular size. To examine how
280 much of an error this assumption introduces into the
281 vaporization enthalpy that is calculated, the data were
282 adjusted in the following manner. First, it was assumed
283 that the detector response was linear with carbon
284 number. In addition, it was also assumed that the
285 retention time of a component was related to the
286 number of C atoms. Although this is not strictly true
287 when comparing aromatic to aliphatic components with
288 the same number of C atoms, this is a reasonable
289 approximation for most linear molecules, as illustrated
290 by Figure 6. This figure correlates the number of C
291 atoms (N_{C}) with the $\ln(1/t_a)$ value of the standards at
292 $T = 359 \text{ K}$. The linear hydrocarbons correlate nicely;
293 only naphthalene is significantly off the line. Generally,
294 aromatic compounds have somewhat longer retention
295 times than the corresponding acyclic hydrocarbons with
296 equal carbon numbers. Hydrocarbons with branching
297 are usually slightly less retained, relative to the n -
298 alkanes. The slope and intercept of the correlation in
299 Figure 6 was used to calculate the hypothetical number
300 of C atoms present in each component of the RP-1 fuel,

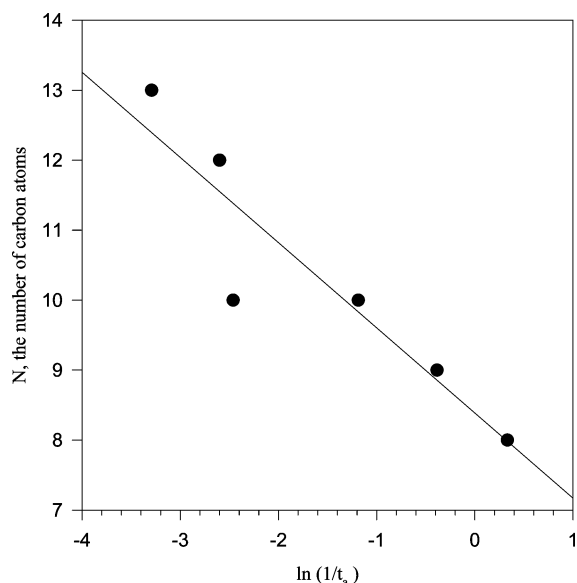


Figure 6. Correlation observed between the number of C atoms present in the standards and the natural logarithm of the reciprocal of their adjusted retention time $\{\ln(1/t_a)\}$ at $T = 364 \text{ K}$. The slopes and intercepts of these correlations are given in Table 4.

based on the observed retention time. The analytical 301
expression used to calculate the adjusted mole fraction 302

Table 4. Slope and Intercept Obtained by Correlating the Number of Carbon Atoms of the Standards (N_C) Used in the RP-1, JP-7, and JP-8 Fuels with the Corresponding Value of $\ln(1/t_a)$ of Each Standard, as a Function of Temperature

RP-1 Fuel			JP-7 Fuel			JP-8 Fuel		
temperature, T (K)	slope, $S(T)$	intercept, $b(T)$	temperature, T (K)	slope, $S(T)$	intercept, $b(T)$	temperature, T (K)	slope, $S(T)$	intercept, $b(T)$
364.0	-1.218	8.39	375.15	-1.5635	8.6631	384.4	-1.5927	9.1355
369.1	-1.240	8.58	380.25	-1.6044	8.9117	389.5	-1.6259	9.3621
374.2	-1.266	8.75	385.25	-1.6484	9.1427	404.9	-1.7175	10.076
379.3	-1.282	8.97	390.45	-1.6925	9.3803	409.9	-1.7443	10.325
384.3	-1.308	9.16	395.75	-1.7352	9.6387	414.9	-1.7779	10.559
			399.35	-1.777	9.9005			

Table 5. Comparison of Vaporization Enthalpies of RP-1, JP-7, and JP-8 Fuels with Literature Values

fuel	approximate formula	approximate formula mass ^a (g/mol)	$\Delta_f^{\#}H_m(298.15\text{ K})$ (kJ/mol)	$\Delta_f^{\#}H_m(298.15\text{ K})$ (kJ/kg)	
				calculated value	literature value(s)
RP-1	$C_{12}H_{23.4}$	167.4	51.5	308	291, 246 ^b
JP-7	$C_{12}H_{25}$	169	55.9	331	330 ^c
JP-8	$C_{11}H_{21}$	153	65.4	428	

^a Data taken from ref 11. ^b Data taken from ref 17. ^c Data taken from ref 18.

303 of each component (n_{ai}) is given by eq 8.

$$n_{ai} = \frac{[n_i/N_C]}{\sum n_{ai}} = \frac{n_i/\{S(T)\ln(1/t_a) + b(T)\}}{\sum n_{ai}} \quad (8)$$

304 The slope ($S(T)$) and intercept ($b(T)$) are functions of
 305 temperature; the values of $S(T)$ and $b(T)$ obtained from
 306 the standards and used for the RP-1, JP-7, and JP-8
 307 fuels are reported in Table 4. The corresponding value
 308 of $\sum n_{ai} \ln(1/t_{ai})$ calculated for the RP-1 fuel at each
 309 temperature using this approximation for detector bias
 310 is given as the last entry at the bottom of the data sets
 311 in Table 1 at each temperature. The solid circle symbols
 312 in Figure 5, which are barely noticeable, illustrate the
 313 correlation of $\sum n_{ai} \ln(1/t_{ai})$ with $1/T$. The last two entries
 314 in Table 3 summarize the vaporization enthalpy calcu-
 315 lated for the RP-1 fuel without and with detector bias.
 316 Adjusting for detector bias in this manner does not seem
 317 to have a significant effect on the magnitude of the
 318 vaporization enthalpy. Similar results, which are also
 319 summarized in Table 5, were obtained for the JP-7 and
 320 JP-8 fuels. The effect of detector bias seems greater for
 321 JP-8, presumably because of the broader range of
 322 molecular size present in this fuel.

323 Discussion

324 One of the approximations inherent in the procedure
 325 described previously is that the enthalpy of mixing is
 326 relatively small and is not likely to introduce a sub-
 327 stantial error in the determination. This is probably a
 328 good approximation for hydrocarbons but may be inap-
 329 propriate for some mixtures. The enthalpies of solution
 330 of hydrocarbons are small and have a tendency to be
 331 slightly endothermic.¹⁵ A characteristic of correlation-
 332 gas chromatography is that, if the vaporization enthal-
 333 pies of pure materials are used as standards in the
 334 correlation, then the results obtained for mixtures will
 335 be for ideal solutions. Given a slightly endothermic
 336 enthalpy of mixing, as would be expected for hydrocar-
 337 bon fuels, the vaporization enthalpy of the mixture is
 338 likely to be slightly smaller than the value obtained by
 339 this technique. A comparison of the vaporization en-

thalpy measured on the mixture by Calvet calorimetry 340
 to the results obtained by correlation-gas chromatog- 341
 raphy would be a direct method for evaluating the 342
 enthalpy of mixing of the hydrocarbons in fuels. This 343
 protocol has been used to evaluate enthalpies of mixing 344
 in other systems.¹⁶ 345

346 Given this approximation, a comparison of vaporiza-
 347 tion enthalpies of the fuels studied with literature
 348 values is given in Table 5. The difficulty already noted
 349 is that typical values for these fuels are not readily
 350 available, and, for those that are available, it is not clear
 351 whether the values are experimental or estimated.
 352 Table 5 summarizes the values that we have been able
 353 to locate. We have not been able to locate any data for
 354 the JP-8 fuel. Agreement for the JP-7 fuel is good,
 355 particularly considering the assumption regarding the
 356 enthalpy of mixing. The results obtained in this study
 357 for the RP-1 and JP-8 fuels do warrant some additional
 358 comments, given the differences that are observed in
 359 Table 6 between the average molecular formula reported
 360 for these fuels, the value of the vaporization enthalpy
 361 estimated, and the magnitude of the vaporization en-
 362 thalpies obtained.

363 Table 6 lists some of the physical properties that are
 364 available for a series of rocket and jet fuels whose
 365 vaporization enthalpies have been measured. The en-
 366 thalpy values can be compared with the predictions of
 367 the following simple empirical relationship that has

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Table 6. Comparison of Various Physical Properties of Some Jet and Rocket Fuels with Literature Values^a

property	Value				
	JP-10 fuel	RJ-4 fuel	RP-1 fuel	JP-7 fuel	JP-8 fuel
H/C ratio	1.6 ^b	1.67 ^b	1.95	2.083	1.91
approximate formula	C ₁₀ H ₁₆	C ₁₂ H ₂₀	C ₁₂ H _{23.4}	C ₁₂ H ₂₅	C ₁₁ H ₂₁
boiling point range (°C)	182–183 ^c	207–221 ^c	177–274	189–251 ^c	177–274
<i>n</i> -paraffins (%)	0 ^d	0 ^e	2.1	8.8	60 ^f
iso-paraffins (%)	0 ^d	0 ^e	27.1	29.1	60 ^f
naphthenes (cycloparaffins) (%)	100 ^d	100 ^e	62.4	59.8	20
aromatics (%)	0 ^d	0 ^e	8.4	2.3	17
Δ _f ^g H _m (298 K) (kJ/mol)					
experiment	49.1 ± 2.3 ^d	55.3 ± 0.3 ^e	51.5 ± 1.2 ^g	55.9 ± 2.4 ^g	65.3 ± 1.0 ^g
calculated ^h	49.9 ± 1.0	59.3 ± 1.2	59.3 ± 1.2	59.3 ± 1.2	54.6 ± 1.0

^a Taken from ref 11, unless noted otherwise. ^b Calculated from the molecular formula. ^c Data taken from ref 18. ^d Data taken from ref 19. ^e Data taken from ref 7. ^f Sum of *n*-paraffins and iso-paraffins. ^g Data obtained from this work. ^h Calculated using eq 9 with $N_Q = 0$.

368 been derived to predict the vaporization enthalpies of
369 hydrocarbons:²⁰

$$\Delta_f^g H_m(298.15 \text{ K}) = (4.69 \pm 0.08)(N_C - N_Q) + (1.3 \pm 0.2)N_Q + (3.0 \pm 0.2) \quad (9)$$

370 The terms N_C and N_Q in this equation refer to the total
371 number of carbons and the number of quaternary
372 carbons, respectively. The predicted vaporization en-
373 thalpies in Table 6 are all derived on the assumption
374 that all the hydrocarbon components in these fuels lack
375 quaternary carbons.

376 Predictions of $\Delta_f^g H_m(298.15 \text{ K})$ for JP-10 fuel, which
377 is a mixture of exo-tetrahydrodicyclopentadiene (99.4%)
378 and endo-tetrahydrodicyclopentadiene (0.6%), is very
379 good.¹⁹ A similar prediction for RJ-4 fuel, which is a
380 mixture of various isomers of exo- and endo-dimethyl-
381 tetrahydrodicyclopentadiene, is somewhat larger than
382 that measured experimentally.⁷ These measurements
383 were also conducted using correlation-gas chromatog-
384 raphy. Considering the fact that some of the components
385 present in exo- and endo-dimethyl-tetrahydrodicyclo-
386 pentadiene do contain quaternary C atoms²¹ brings the
387 estimated value more in line with the value measured
388 experimentally. As illustrated in Table 7, branching also
389 reduces the vaporization enthalpy slightly, relative to
390 the value calculated by eq 7. Combined with a small
391 endothermic enthalpy of mixing, the estimated and
392 experimental values for RP-1 seem to be internally
393 consistent, within the uncertainties stated.

394 The vaporization enthalpy predicted for the RP-1 fuel
395 is also greater than that measured experimentally, by

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Table 7. Comparison of Experimental and Estimated Vaporization Enthalpies of Some Aliphatic and Aromatic Compounds

hydrocarbon	Δ _f ^g H _m (298.15 K) (kJ/mol)		
	experiment	calculated ^a	reference
Aliphatic Hydrocarbons			
hexane	31.6	31.1	13
2-methylhexane	34.9	35.8	13
2,4-dimethylhexane	37.8	40.5	13
2,5-dimethylhexane	37.9	40.5	13
decane	51.4	49.9	13
2-methyldecane	51.9	54.6	13
dodecane	59.5	59.3	13
Aromatic Hydrocarbons			
benzene	33.8	31.1	13
toluene	38.0	35.8	13
<i>o</i> -xylene	43.4	40.5	13
ethylbenzene	42.2	40.5	13
naphthalene	56.7 ^b	49.9	22
1-methylnaphthalene	61.1	54.6	23
biphenyl	64.9	59.3	24

^a Calculated using eq 9 with $N_Q = 0$. ^b Adjusted to $T = 298.15 \text{ K}$ from $T = 417 \text{ K}$ using an estimated value for $C_{pl,m}$ of $205 \text{ J mol}^{-1} \text{ K}^{-1}$ and the following equation (from ref 25): $\Delta_f^g H_m(298.15 \text{ K}) (\text{kJ/mol}) = \Delta_f^g H_m(T_m) + [(10.58 + 0.26C_{pl,m})(T_m - 298.15)]/1000$.

Table 8. Summary of Some Physical Properties of the RP-1, JP-7, and JP-8 Fuels Evaluated in This Study

property	Value		
	RP-1	JP-7	JP-8
H/C ratio	2.045 ± 0.1	2.049 ± 0.02	1.95 ± 0.07
average MW	148 ± 9	166 ± 1	160 ± 3
approximate formula	C _{10.6} H _{21.7}	C _{11.8} H _{24.2}	C _{11.5} H _{22.4}
Δ _f ^g H _m (298 K) (kJ/mol)			
experiment	51.5 ± 1.2	55.9 ± 2.4	65.3 ± 1.0
calculated ^a	52.7 ± 1.2	58.3 ± 1.2	56.9 ± 1.2

^a Calculated using eq 9 with $N_C = 10.6$ for RP-1, 11.6 for JP-7, and 11.5 for JP-8; $N_Q = 0$ for all fuels tested.

(7.8 ± 1.7) kJ/mol. A large H/C ratio and the NMR ratio
of aromatic CH to aliphatic CH ($1/_{119}$) for the RP-1 fuel
suggests the presence of very few aromatic components.
The composition of the RP-1 fuel in Table 6, as obtained
using GC/MS, concurs with this analysis.¹¹ A low
occurrence of *n*-paraffins (2%) and aromatics (8.4%), but
a much larger occurrence of iso-paraffins (27%) and
naphthenes (cycloparaffins, 62.4%), has been reported.
The H/C ratio measured in this study (Table 8) is
somewhat larger than the literature value. Both are
reasonably consistent with a low occurrence of aromatic
hydrocarbons. As illustrated in Table 7, the presence

of highly branched hydrocarbons, including some with quaternary carbons, would be expected to reduce the experimental value, relative to the value predicted by eq 9. However, even with a small endothermic mixing term, it is not clear whether the reduction would amount to the 7.8 ± 1.7 kJ/mol difference that is observed. The retention time data for the RP-1 fuel (see Figure 1), relative to the JP-7 and JP-8 fuels (see Figures 2 and 3) suggests an average carbon content that is slightly less than that reported in Table 6. However, this possibility does not seem to be supported by the boiling point range. To test whether a slightly smaller molecular weight is responsible for the smaller vaporization enthalpy measured, the equations listed in Table 4 for the RP-1 fuel were used to evaluate an approximate average molecular weight. These equations relate retention times to the number of C atoms of the standards. As a means of evaluating an average molecular weight, these equations, along with the GC retention times, were used to evaluate the number of C atoms of each analyte in the RP-1 fuel. Combining the adjusted mole fraction of each analyte as reported in Table 1, the average experimental H/C ratio reported in Table 8, and summing over all analytes, eq 10 provides a means of evaluating an average molecular weight:

$$\begin{aligned} \text{MW} &= \sum (n_{ai}) N_{Ci} \{12 + (\text{H/C})\} \\ &= \sum (n_{ai}) \{S(T) \ln(1/t_{ai}) + b(T)\} \{12 + (\text{H/C})\} \end{aligned} \quad (10)$$

The molecular weight results obtained for the RP-1 fuel are summarized in Table 8. An average molecular weight of 148 ± 9 , combined with the H/C ratio of 2.045 measured by NMR, results in an average molecular formula of $\text{C}_{10.5}\text{H}_{22.5}$. The uncertainty in the molecular weight was obtained from the standard deviation in the molar mass associated with using each of the equations in Table 4 that have been evaluated for the RP-1 fuel. If the molar mass evaluated in this manner is a reasonable value for this sample of RP-1 fuel, then the experimental and estimated values listed in Table 8 for this formula are in good agreement.

Our GC/MS results on JP-7 fuel and those previously reported⁴ clearly indicate the presence of significant amounts of *n*-paraffins (8.8%). A large composition of iso-paraffins (29.1%) and naphthenes (59.8%), coupled with a low content of aromatics (2.3%), have been reported. Our NMR results are also consistent with a small ratio of hydrogens on sp^2/sp^3 carbons ($1/_{831}$). In this case, branching and the presence of an occasional quaternary carbon, combined with a small endothermic enthalpy of mixing, would bring the predicted and experimental values well within their range of uncertainty. JP-7 fuel also provides a good test case of how well molecular weights can be determined using GC retention times. Using the H/C ratio, as determined by NMR, the average molecular weight and molecular formula of the JP-7 fuel was determined using eqs 10

and 4, as described for the RP-1 fuel. A molecular weight of 166 ± 1 amu and a molecular formula of $\text{C}_{11.8}\text{H}_{24.2}$ were obtained, which are in very good agreement with the literature.

The experimental vaporization enthalpy of the JP-8 fuel is more problematic. As suggested by the experimental vaporization enthalpies of some of the aromatic compounds likely to be found in JP-8 fuel (see Table 7), experimental vaporization enthalpies of fuels that contain significant amounts of aromatic hydrocarbons are likely to be larger than the values estimated. However, the contribution of these differences when combined with a small enthalpy of mixing, which probably attenuates these differences, is not likely to account for all of the 9.8 kJ/mol difference observed between experimental and estimated values. The vaporization enthalpy is reproducible. A duplicate analysis of JP-8 resulted in a vaporization enthalpy of 64.8 ± 1 kJ/mol (data not shown). Comparison of the boiling temperature range of JP-8 fuel, the *n*-paraffin composition, and the relative retention times of the components in JP-8 fuel, relative to the RP-1 and JP-7 fuels (see Figures 1–3), suggested that the average molecular weight of the JP-8 fuel may be slightly larger than the literature value.¹¹

Application of the same NMR and molecular weight protocol to the JP-8 fuel resulted in a H/C ratio of 1.95 and an average molecular weight of 160 ± 3 amu. This results in an average molecular formula of $\text{C}_{11.5}\text{H}_{22.4}$, which, again, is in good agreement with the literature. Although these results reduce the difference between experimental and estimated values to 8.4 ± 1.6 kJ/mol, the chemical composition of JP-8 fuel alone does not seem to be able to bring the estimated and experimental vaporization enthalpy values completely in line with expectations.

Conclusions

The vaporization enthalpies of RP-1, JP-7, and JP-8 fuels have been measured by correlation-gas chromatography. The values obtained for the RP-1 and JP-7 fuels are consistent with values available in the literature and with those estimated. The average composition of these fuels has been estimated using NMR and gas chromatography. Given the molecular complexity and variability of these fuels, the results seem to be in good agreement with literature values.

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Supporting Information Available: Retention times, as well as details regarding (H/C) analyses, are included (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.